QUANTITATIVE DETERMINATION OF METALS CONTAINING OXIMES

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Except the alkaline metals and alkaline-earth metals and some heavy metals such as Pb, Fe, etc the majority of elements within this class emerge in small amounts, dispersed in natural backgrounds, in raw materials, deposits, industrial waters, dead catalysts and not ultimately in rivers basin, lakes and oceans. Presently, trials are being more and more intensively undergone for their isolation and concentration as well as for rare metals recovery, which are expensive. In order to solve these issues researchers shall widely resort to the use of different types compounds, among which the oximic derivatives are to be found. The intended outcome for the accomplished theoretical and experimental researches is to provide the possibilities for the use of oximes as precipitating reagents and the determination of some metals within the analytical practice.

In the present work there are shown physico-chemical characterization with middle transformation IR spectra, TG, DTA, and DTG measurements studies the thermal behavior of the nickel (II) chelates with asymmetric -dioximes. These complexes have a great importance from the analytical methods for determining the metal mentioned under this form.The work presents also the spectrometric methods for determining the nickel with aliphatic asymmetric dioximes, namely the methyl-ethyl-dioxime, respectively methyl-isopropyl-dioxime.

The statistical interpretation of the experimental data, in comparison with other methods which are known in the literature and we specially refer to the determinations based upon the reaction of nickel with dimethylgioxime certify that the worked out methods of the present work are enough accurate and reproducible for the purpose we have in view. The asymmetric dioximes may set up potential organic reagents in the analytic determinations of nickel and palladium, as they are extremely sensitive and selective for this metal.

Keywords: *aliphatic asymmetric dioximes, methods of analysis, spectrometric methods.*

The oximes compose anionic and cationic chelated compounds, generally water-soluble, which could be extracted from the aqueous phase by means of polar organic solvents, immiscible with water. Another group of metal oximates present a non-electrolytic characteristic, are water-insoluble and soluble in non-polar solvents: saturated hydrocarbons, unsaturated hydrocarbons or halocarbons (per fluorocarbons, partly or totally chlorinated hydrocarbons), and in consequence they could be extracted from the watery environment. The extraction represents a basic process within the hydroelectric plant of low head for some transition metals.

The modern chromatographic methods also make use of different oximes used for recovery and concentration of metals from the mixtures they initially form. A series of ion-exchange resins have been obtained through polycondensation or copolymerization processes from unsaturated hydrocarbons, aldehydes and cetones by composing oximic groups under the presence of hydroxylamine, respectively under isonitrosation. The columns filled with such resins are used nowadays with promising results for dissociation and concentration of precious metals found in the oceans or in the ashes resulting from the steam power plants.

For the purification of some reagents, for example by removing the remains of transition metals from the 3d and 4d groups, chromatographic columns are sometimes used with fillings also containing □-ketoximes, respectively □-dioximes [1,2].

Thin-layer chromatography (by using silica, alumina and silica gel layers in different proportions, especially pre-treated) allows for the chemical separation and identification of some transition metals from biological samples. The specific reagents: □-dioximes, □-ketoximes, hydroxyoximes, etc. are included within the mobile phase or development substances. Generally, the values of the R_f-es (Rutherfordium) obtained exceed 0,1-0,2 allowing for objective analytical interpretations [3].

METHODS OF ANALYSIS

The most common methods directed towards this purpose are gravimetric, volumetric (alkalimetry, volumetric methods based on oxidation-reduction chemical reactions), electrochemical (potentiometry, polarography) and spectrometric methods within the visible and ultraviolet domain.

The selection of analysis method depends on the concentration of the respective metal encountered in the sample composition, on the specificity of its chemical reaction with oximes, as well as on the nature of other accompanying metals present in the sample. One should also take into consideration the physical and chemical properties of the oximate as a determination test (solubility, heat endurance, dyeing intensity, etc). For analytical objectives □-dioximes, hydroxyoximes (acyloinoximes, salicyloximes) are generally employed and also nitroso-phenols and nitroso-naphthols. Composite oximes with Schiff base are mostly used for structure studies (RES, RMN, X-rays etc) their analytical importance being insignificant [4,5].

Direct volumetric methods are based on oximes chemical reactions by forming hardly soluble precipitates. The aqueous solution of the salts contained in metals is being titrated with the solutions of addendum ligatures at optimum pH in order to conceive hardly soluble compounds.

Indirect volumetric methods

The chemical reaction of oximes with metallic ions is accompanied by the release of hydrogen ions:

$M^{2+} + 2Diox.H_2 = M(Diox.H)_2 + 2H^+$
M = Ni, Co, Pd, Pt, Cu, Cd etc.

The compounds thus obtained which are water-soluble or insoluble are generally intensely coloured. For this reason, when titration with NaOH of the released H^+ ions takes place, acidic and basic external indicators shall not be used (methyl orange, methyl red, phenolphthalein etc), but researchers resort instead to the determination of equivalence point using the potentiometric method.

An important indirect method is represented by the oxidimetric determination of the hydroxylamine formed subsequent to the oximic compounds hydrolysis [6].

For achieving a total hydrolysis the compounds samples are boiled for some 20-30 minute-period using an excess of diluted H_2SO_4. The hydrolysis conducts to the formation of different cetones and free hydroxylamine.

For oxidimetric titrations solutions of $KMnO_4$, $K_2Cr_2O_7$, $KBrO_3$, KIO_3, $Ce(SO_4)_2$, $NaVO_3$, BrCl etc. are being used.

The chemical reactions that occur within the oxidimetric titrations are rendered by the following equations:

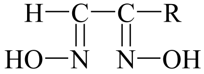
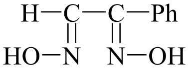
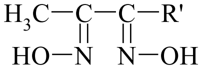
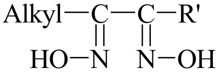
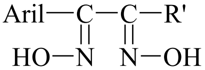
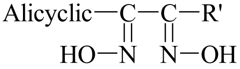
$$BrO_3^- + H_2N{-}OH \rightarrow Br^- + H_2O + NO_3^- + H^+$$

$$6Ce^{4+} + H_2N{-}OH + 2H_2O \rightarrow 6Ce^{3+} + NO_3^- + 6H^+$$

$$H_2N{-}OH + 3BrCl + 2H_2O \rightarrow HNO_3 + 3HBr + 3HCl$$

Table 1

Structure of some asymmetric α -dioximes.

Structure of dioxime	Kind of R, respectively R' radicals
 $\begin{array}{c}H{-}C{-}C{-}R\\ \Vert \quad \Vert\\ HO{-}N \quad N{-}OH\end{array}$	R = CH_3 - ; C_2H_5 - ; n - C_3H_7; i-C_3H_7 ; n - C_4H_9 ; i - C_4H_9, etc.
 $\begin{array}{c}H{-}C{-}C{-}Ph\\ \Vert \quad \Vert\\ HO{-}N \quad N{-}OH\end{array}$	Ph = C_6H_5 - ; X - C_6H_4 - ; $C_{10}H_7$ -
 $\begin{array}{c}H_3C{-}C{-}C{-}R'\\ \Vert \quad \Vert\\ HO{-}N \quad N{-}OH\end{array}$	R’ = C_2H_5 - ; n - C_nH_{2n+1}; i - C_nH_{2n+1}
 $\begin{array}{c}Alkyl{-}C{-}C{-}R'\\ \Vert \quad \Vert\\ HO{-}N \quad N{-}OH\end{array}$	R' = aril, heterocyclic or alicyclic radical
 $\begin{array}{c}Aril{-}C{-}C{-}R'\\ \Vert \quad \Vert\\ HO{-}N \quad N{-}OH\end{array}$	R' = heterocyclic radical
 $\begin{array}{c}Alicyclic{-}C{-}C{-}R'\\ \Vert \quad \Vert\\ HO{-}N \quad N{-}OH\end{array}$	R' = heterocyclic radical (heteroatom: O, S, Se, N, P etc.)

Spectometrical methods for analysis

Most of α-substituted oximes of different types, as well as some poly-oximes provide intense dyeing within aqueous solutions and in polar or apolar organic solvents, depending on electric load, and sometimes depending on the nature of addendum ligature of the respective compounds. However, the solubility of these metallic derivatives encoding different tags within organic and aqueous phase provides selective extraction possibilities for chelate-compounds depending on the aqueous solutions pH.

The great chemical stability of these derivatives, especially within organic phase, results from spectrometric measurements. Their coloured solutions comply with Lambert-Beer Law within a concentration domain ranging between 10^{-4} and $4\text{-}6\cdot10^{-3}$, depending on their molar absorption coefficient. In order to perform analytical studies, calibration curves are being used which are regular lines for the most part. Linearization diversions might appear sometimes which indicates either dissociation, either a molecular association.

Several studies with reference to the value of distribution coefficient (D_A) between organic and aqueous phase have been issued within the specialized literature, depending on the nature of radicals connected to simple functional oximic groups and □-substituted groups (radicals which could be aliphatic, alicyclic, aromatic, heterocyclic, with shorter or longer carbon chains), on the essential characteristics and stability of hydrogen intramolecular and intermolecular interactions, and on their solvation possibilities. All these phenomena influence, to a certain extent, the effectiveness of compounds extraction process.

In the case of chemical anionic and cationic chelates, superior alcohols are used for extraction, non-miscible with water: n - and i - butanol, hexanol, pentanol, different types of esters.

For spectometrical determination by means of oximes for some transitional polyvalent metals in compositions, it is sometimes recommended their initial dissociation from accompanying metals. A classical example consists in the dissociation of ruthenium and osmium subsequent to vapour distillation under the form of RuO_4 and OsO_4. Spectometrical determination by means of oximes is performed within a reducing environment

RESULTS AND DISCUSSION

The classical reagent employed for the quantitative determination of Ni (II) ions is dymethylglioxime. It has been ascertained that the Ni (II) ions are easily precipitating also with asymmetrical dioximes *(tab.1)*, in slightly alkaline solutions and are forming heavily soluble compounds whose physical and chemical properties are very profitable from an analytical point of view [7,8].

The thermo gravimetric measurements shows that these substances have a considerable heat resistance and are easily soluble in polar organic solvents which allow the nickel weigh batching and spectrometer nickel batching.

The study of thermal decomposition by using the TG, DTA and DTG methods *(fig. 1).*of the compound [Ni (Me-Et-Diox.H)$_2$] is presented in this paper.

The Ni(II) dioximates with different asymmetrical □ -dioximes present remarkable heat endurance. Except the most elementary representative [Ni (DMGH)$_2$].H_2O, those with asymmetrical dioximes do not contain crystal water and generally decompose at temperatures exceeding 170 - 200°C.

This phenomenon is very important from an analytical point of view and it should be taken into consideration at the elaboration of gravimetric methods for the determination of Ni (II) under this form. On the basis of thermal analysis (TG, DTA, DTG) a temperature interval, usually between 130 - 160° C could be recommended for oven drying of precipitates.

Characterization of nickel complexes with asymmetric dioximes. IR spectra

The use of asymmetric dioximes in the coordinative and analytic chemistry rises a series of structural problems. In case of square-plane and octahedral complexes of transitional metals with asymmetric dioximes, new isomeric combinations may be set up. On the plane derivatives there is "cis-trans" geometric isomery *(fig. 2).* On the "cis" isomers, where the two R, respectively R' groupings occupy a field-way position in the molecule and around the metallic central atom, a local C_{2v} symmetry is risen. On the "trans" isomer, the R, respectively R' groupings are situated in the opposite corners of the square. In this case, the local symmetry shall be C_{2h}.

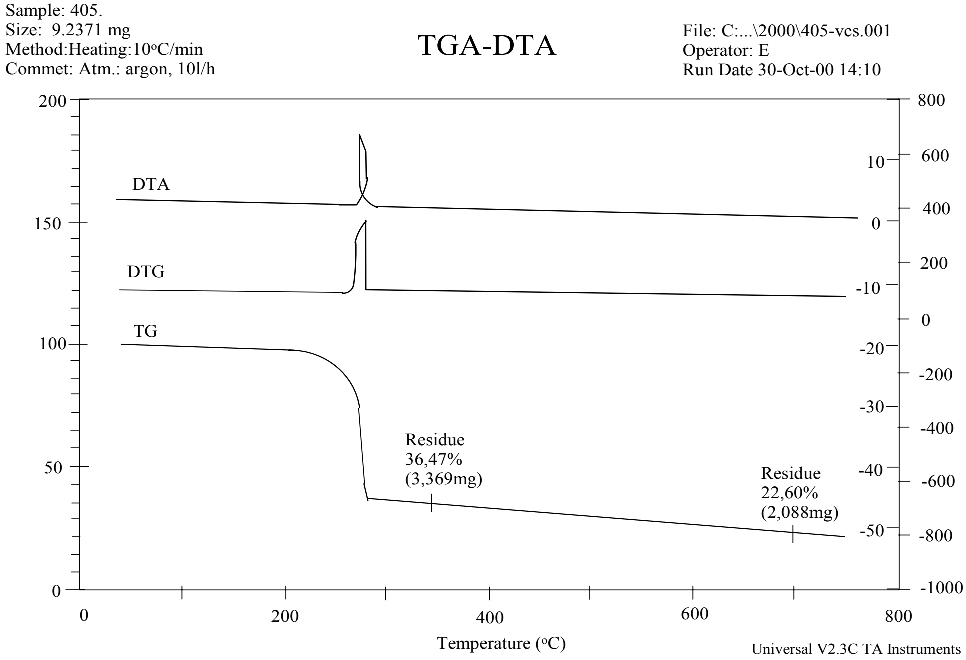
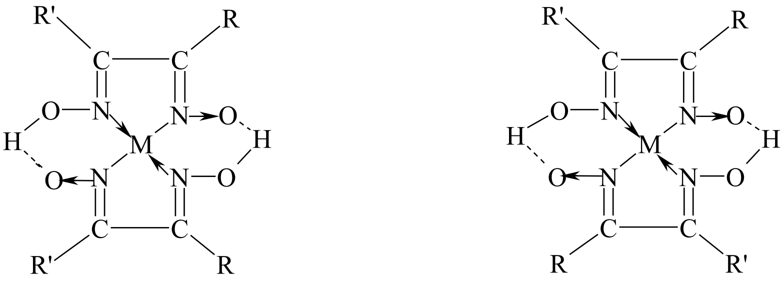


Figura 1. **Thermo-analytical curves of the compound [Ni (Me-Et-Diox.H)$_2$].**

Both the chemical and physico-chemical characterization of nickel complexes with asymmetric dioximes is carried out by modern methods of analysis, namely infrared absorption spectrometrics (IR). The study of infrared absorption spectrometrics *(tab. 2)* of the compound [Ni (Diox.H)$_2$] is presented in this paper.



„cis” „trans”

Figura 2. **Square-plane structure of complexes with asymmetric dioximes.**

Table 2

Characteristic IR vibrations of the Ni(II) complexes with asymmetric α-dioximes.

Characteristic vibrations	Wave number of the IR band (1/cm)		
	$[Ni(DMGH)_2]$	$[Ni(Me\text{-}Et\text{-}Diox.H)_2]$	$[Ni(Me\text{-}i\text{-}Prop\text{-}Diox.H)_2]$
ν (C – H)$_{as}$ (aliphat)	2965(I)	2966(i)	2981(i)
ν (C – H)$_s$ (aliphat)	2930(I)	2934(i)	2941(i)
ν (C – H)$_{as}$ (aliphat)	2860 (m)	2876 (m)	2880 (m)
δ (O – H…O)	1720 – 1750 (s)	1730 – 1760 (m)	1750 – 1780 (m)
ν (C = N)	1560 (fi)	1562 (fi)	1564(fi)
δ (CH$_3$)$_{as}$	1440 (fi)	1454 (fi)	1460 (fi)
δ (CH$_3$)$_{as}$	1386 (fi)	1367 (fi)	1366 (i)
ν (NO)	1235 (fi)	1234 (fi)	1235 (fi)
ν (NO)	1090 (fi)	1077 (i)	1110 (fi)
δ (CH$_3$)$_r$	1030 (I)	1035 (i)	1040 (i)
δ (OH)$_r$	960 (I)	976 (fi)	968 (m)
δ (CH$_2$)$_r$	753 (I)	754 (i)	752 (m)
δ (CNO)	730 (fi)	740 (fi)	735 (i)
ν (Ni – N)	519 (fi)	516 (fi)	513 (fi)
δ (skeleton)	429 (fi)	426 (fi)	427 (fi)
δ (skeleton)	385 (m)	395 (i)	380 (m)
δ (C = N)$_t$	187 (I)	175 (fi)	175 (i)
δ (CH$_3$)$_t$	269 (m)	270 (i)	266 (m)
δ (N – Ni – N)	210 (m)	205 (m)	202 (m)

Spectrometric Determination of Ni (II) with Aliphatic Asymmetric Dioximes

The following asymmetrical dioximes have been employed for the spectrometric determination of Ni (II): methyl-ethyl-dioximeand methyl-isopropyl-dioxime. In order to extract the compounds with a non-electrolytic characteristic, of the type: $[M(Diox.H)_2]$; M = Ni, Pd, Pt unsaturated and saturated chlorinated hydrocarbons are being used (benzene, phenyl methane, xylene, dichloroethane, chloroform, carbon dichloride, tetrachloroethane).

In this paper is presented the field of concentration the Lamber-Beer law and values of absorption molar coefficients are checked up under in the case of carried out determinations *(tab. 3)*.

Table 3

Linear concentration field and value of absorption molar coefficient in the determinations of Ni(II) with aliphatic dioximes.

Studied metallic complex	Linear concentration field (mg Ni)	Absorption molar coefficient ε (L/cm.mol)
[Ni(methyl-ethyl-diox.H)$_2$]	0.0880-0.6216	244.251
[Ni(methyl-i-propyl-diox.H)$_2$]	0.0816-0.5712	266.369

The data of the analysis performed display the fact that the employed asymmetrical dioximic reagents are sensitive and selective for the determination of Ni (II).

CONCLUSIONS

Starting from a wide range of applications for the compounds within the oxime class, employed as extraction agents in the domain of hydroelectric plant of low head or as addendum highly selective ligatures that compose some ion-exchange resins, we consider that a thorough study of the oximic structures shall give the possibility of new applications discovery for this class of compounds.

The study of thermal decomposition of some nickel compounds with asymmetrical dioximes showed an increased heat endurance of these compounds which do not contain crystal water and generally decompose at temperatures exceeding 170-200°C. These characteristics of asymmetrical dioximates have a great significance analytically speaking, as they constitute important parameters for the elaboration of gravimetric methods in order to determine different metals under this form.

Organic phase extracts of dioximates compounds spectrometrically analyzed allow the quantitative determination of different metals, especially nickel. Statistic experimental data processing draws to the conclusion that the proposed methods for the nickel gravimetric and spectrometric determination, using the dioximic reagents synthesized and employed for the first time in this purpose, are precise and reproducible.

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